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## Advanced fuels and engines workshop brings together research, fuel, and engine communities

Sandia's Hub for Innovation in the Transportation Energy Community (HITEC), with the CRF at its core, hosted its first workshop November 16-18 in San Ramon. The workshop, named "Next Generation Biofuels and Advanced Engines for Tomorrow's Transportation Needs," brought together representatives from engines and fuels industries, academia, national laboratories, and other research organizations. The event was supported in part by Chevron Corporation.

"What's really fascinating and exciting for me is the demographics in the room," said Vice President Rick Stulen in his opening remarks. "Perhaps for the first time, we are seeing three communities represented that don't always spend a lot of time together—the research community, the fuel community, and the engine community. It's the sort of the conversations that happen in these group settings that, in my experience, often lead to very exciting results."

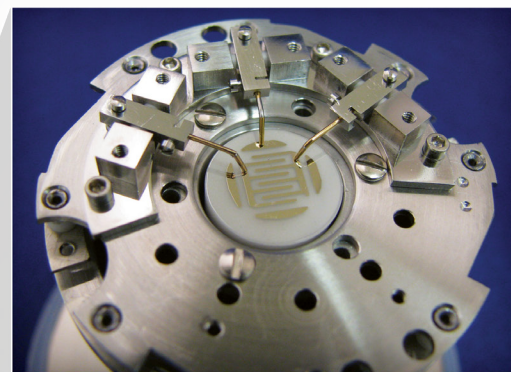
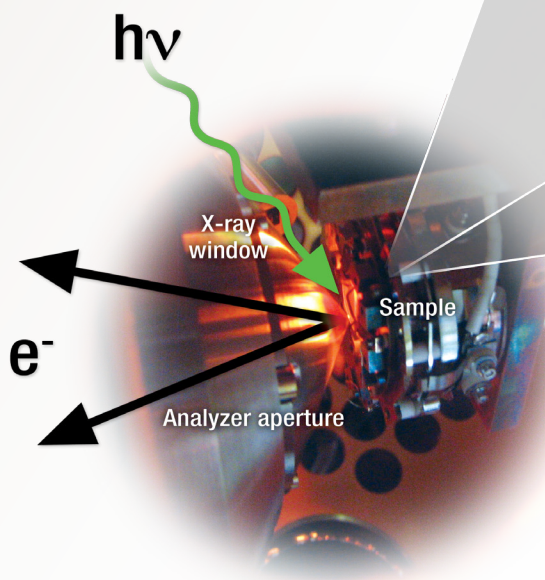
Bob Carling, director of the Transportation Energy Center, noted the daunting challenges ahead for everyone in the room in terms of energy security and climate change. "There are some strict and compelling regulations set for the

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## Investigating surface electrochemistry using synchrotron radiation and ambient pressure photoemission spectroscopy

The development of advanced technologies for energy storage and utilization is widely recognized as critical to establishing a secure and sustainable energy portfolio in the U.S. Research efforts currently favor electrochemical systems that utilize devices such as super capacitors, batteries, and fuel cells because of their inherently high efficiencies and compatibility with existing electrical energy generation and fuel-delivery infrastructures. The essential physical phenomenon that occurs in all electrochemical-based devices is the transfer of electrical charge across a material interface.

Mechanisms that govern charge transfer are poorly understood, as are the relationships between such phenomena and device performance and reliability. Gaining fundamental knowledge in this regard would enable the development of optimally designed electrode/electrolyte interfaces and thus more efficient or robust technologies.

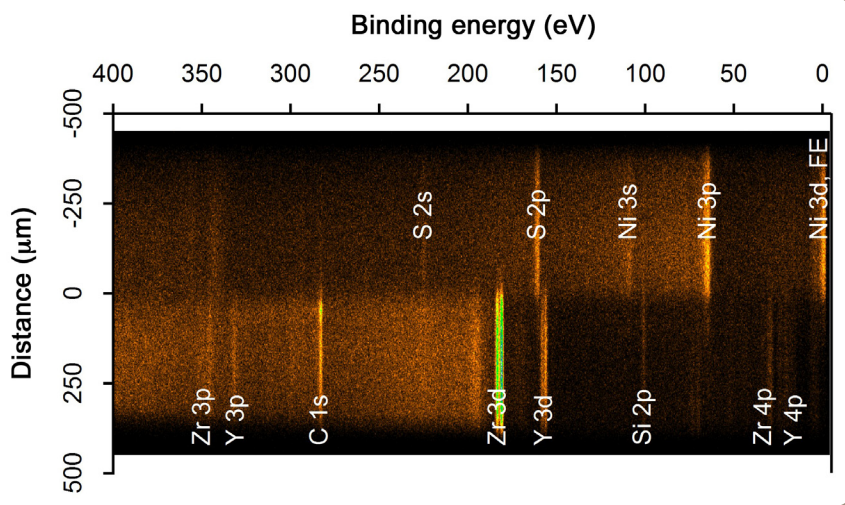


**Figure 1.** A patterned metal electrode sample (inset) mounted in the ALS environmental chamber. The sample is heated to 973 K, and is exposed to synchrotron radiation at x-ray energies below 1000 eV. Photoelectrons are collected through a small orifice placed in close proximity to the surface. Electrical contact to the metal film is maintained by three spring-loaded pins affixed to the face of the sample holder (also pictured in the inset).

Researchers Farid El-Gabaly, Tony McDaniel, Roger Farrow, and Kevin McCarty of Sandia, along with beamline scientists Michael Grass, Zhi Liu, and Hendrik Bluhm of the Advanced Light Source (ALS) department at Lawrence Berkeley National Laboratory have devised an experimental platform to use ambient-pressure photoemission spectroscopy (AP-PES) to directly observe local surface potential, chemical composition, and elemental oxidation states at surfaces and interfaces of solid oxide electrochemical cells (SOEC) during operation. Heretofore, high-temperature electrochemical systems have been difficult to explore *in situ* because of

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**Figure 2.** Spatially resolved image of photoelectron binding energies measured at the interface between the Ni electrode (top portion of figure from 0 and -500  $\mu\text{m}$ ) and the YSZ electrolyte (bottom portion of figure from 0 and +500  $\mu\text{m}$ ). The physical location and surface abundance of compounds containing the elements C, Si, S, Ni, Y, and Zr are easily distinguished by false-colored vertical bands in the image.

difficulties associated with adapting optical and electron-based spectroscopies to the hostile environment, and the demands required to image chemical species on surfaces and at interfaces under relevant operating conditions.

Ambient pressure operation is a major advance in the application of photoemission spectroscopy (PES) to the analysis of catalytic surfaces (Bluhm, H. et al. *MRS Bulletin-Materials Research Society* **32**, 1022 [2007]). In more conventional, laboratory-based PES the operating pressure is restricted to ultra-high vacuum because the mean free path of the ejected electron is much shorter than the flight path to the energy analyzer.

As such, it is always questionable if observations conducted on quenched surfaces at ultra-high vacuum are representative of these same surfaces under high adsorbate flux; such discrepancies give rise to the well-known “vacuum gap” in material science. Furthermore, for an SOEC in an ultra-high vacuum environment, the density of gas-phase molecules is too low to promote electrode reactions needed to generate meaningful electrochemical currents.

### Advancements make *in situ* observation possible

Two key advancements make possible the APPES experiment: (1) collecting photoelectrons near the irradiated surface through a differentially pumped energy analyzer equipped with electron focusing optics, and (2) a high-intensity soft x-ray source produced by synchrotron radiation. Our current work has extended the APPES capability to the *in situ* study of electrochemistry. Salient features of the experimental apparatus are illustrated in Figure 1. Also pictured is an electrochemical cell patterned with Ni and Pt metal electrodes atop a single crystal of yttria-stabilized zirconia (YSZ) electrolyte. The custom hardware that allows us to apply electrical bias and

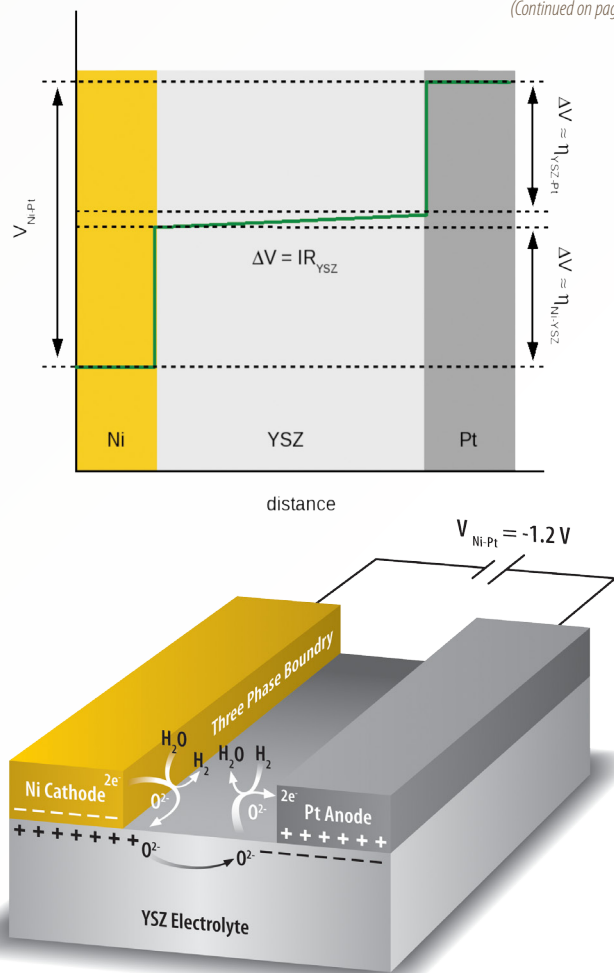
## Investigating surface electrochemistry (cont.)

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perform traditional potentiostatic characterization of devices simultaneously to the XPS was designed by Sandian Josh Whaley.

Figure 2 illustrates a typical PES spectrum that is energy resolved along the x-axis and spatially resolved in one dimension along the y-axis. Here the chemical composition of the surface in the region around the Ni electrode/YSZ electrolyte interface is revealed. Evident in Figure 2 is the boundary between Ni and YSZ, the so called three-phase boundary (TPB), as well as surface contaminants such as sulfur and carbon, which are absorbed locally on the electrode and electrolyte, respectively. The TPB is a region where the electrode, electrolyte, and gas phases coexist; it is important in SOEC electrochemistry because this is the region where charge transfer is assumed to occur.

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**Figure 3.** Diagram of the potential map along the surface between the electrodes under negative polarization as referenced to the Ni electrode (top). The abrupt discontinuity in the surface potential is indicative of the electrode polarization resistance, which is a key variable to understanding charge transfer reactions. Below this is a schematic of the region between two metal electrodes in the patterned film. Ni is separated from Pt by approximately 400  $\mu\text{m}$  of exposed YSZ electrolyte. Water splitting or hydrogen oxidation can occur at either electrode depending on the polarization and magnitude of the applied potential.



## COMBUSTION RESEARCH FACILITY VISITOR PROGRAM

*These visitors will be leaving the Combustion Research Facility at the completion of their tenure.*



### **Bruno Coriton**

Bruno Coriton was a visiting graduate student from Prof. Alessandro Gomez's group at Yale University. He worked with Jonathan Frank in the Advanced Imaging Laboratory using laser-based imaging diagnostics to study flow-flame interactions in turbulent premixed counterflow flames. Bruno and Jonathan used reaction-rate imaging techniques to examine the effects of turbulence on the conversion of CO to CO<sub>2</sub> for different flame stoichiometries.

### **Caspar Christiansen**

Caspar Christiansen, from the Technical University of Denmark, visited Lyle Pickett at the CRF from September 15 to December 15, conducting research on diesel spray combustion. He performed gas temperature measurements in the Engine Combustion Department's constant-volume combustion chamber using fine-wire thermometry and Rayleigh scattering.



### **Andrea Gruber**

Andrea Gruber was a visiting researcher from SINTEF Energy Research, the largest independent research organisation in Scandinavia, from November 30 to December 16. He has been a frequent visitor with Jackie Chen since 2004. Andrea and Jackie collaborated to perform direct numerical simulation of turbulent reactive channel flow to investigate flame-wall interactions.

### **Sigurd Sannan**

Sigurd Sannan, also from SINTEF in Trondheim, Norway, visited Alan Kerstein during the month of November to pursue their ongoing collaborative work on turbulence combustion model development. Details of their work and of the broader context of collaborative research planned between SINTEF and Sandia will be described in a future *CRF News* article.





## Livermore Valley Open Campus on track for fall opening

Plans for the Livermore Valley Open Campus (LVOC), given the green light last August, are proceeding apace. LVOC is a joint proposal between Lawrence Livermore National Laboratory (LLNL) and Sandia National Laboratories to leverage the ground-breaking research of the nuclear security labs through private-sector collaborations.



Led by the CRF's Bob Carling along with counterparts at LLNL, the LVOC initiative is conceived as an 'enabler' that will provide expanded opportunities for research collaborations between Sandia/California, LLNL, and external partners. Anchored by Sandia's CRF on one side and LLNL's National Ignition Facility (NIF) on the other, the LVOC will consist of an approximately 50-acre parcel along the eastern edge of the LLNL and Sandia sites along Greenville Road.

A more open sector, one with fewer security restrictions, will benefit a wide range of potential collaborators including those that focus on high-performance computing, life sciences, optical sciences, and biotechnology, which is especially important as Sandia continues to focus on transportation energy programs.

"If we wanted to arrange a visit to Sandia California next week for Toyota's top executives from Tokyo, for example, we simply couldn't make it happen due to the the badging processes that are in place," Bob Carling says. Though such processes are clearly necessary for both labs' national security mission, Sandia and LLNL both are moving in directions that will require more flexibility, particularly when foreign national and other uncleared visitors are involved.

Several physical changes have already been made to open up the area: the tall fence that partially surrounded the CRF has been taken down (as can be seen in the accompanying photos), the north-east entrance to the complex has been repaved, and the outer guard house has been removed. The bidding process for a new CRF building is nearly complete, and ground-breaking is expected to begin soon.



The LVOC proposal is being developed in parallel with Sandia's Hub for Innovation in the Transportation Energy Community (HITEC) program. Effective access to the international community and greater collaboration with industry are essential to the advancement of HITEC and will be more easily achieved with a successful open campus. The LVOC will be a relatively open sector with fewer security restrictions to impede visits from collaborators from industry and academia.



## Investigating surface electrochemistry (cont.)

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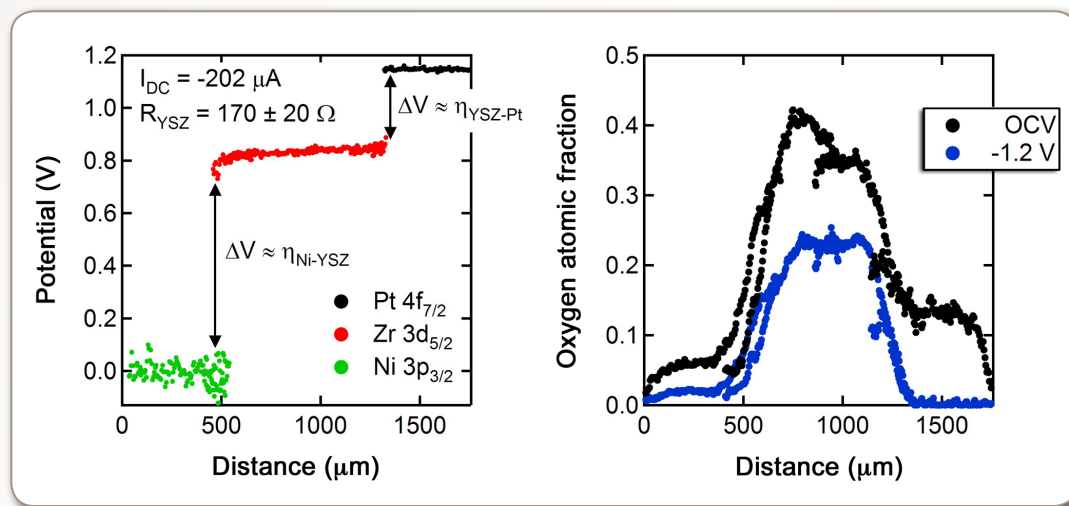
The operation of an SOEC in a single-chamber environment containing water and hydrogen is illustrated conceptually in Figure 3. Here water molecules are reduced at the Ni electrode, which is held at a more negative potential relative to Pt, thus producing hydrogen and a negatively charged oxygen anion ( $O^{2-}$ ). The oxygen anion transports through the YSZ electrolyte driven by a net electrochemical potential gradient established between the Ni and Pt electrodes, and then subsequently reacts with molecular hydrogen at the Pt electrode to produce water.

We are interested in studying the complex interfacial and surface-mediated processes that govern electrode kinetics (i.e., water reduction), formation of the charged double layer, movement of oxygen anion across the double layer, and electron transfer from charge carriers in the YSZ (namely  $O^{2-}$ ) to and from the Ni and Pt electrodes.

### A powerful new approach to investigating surface electrochemistry

APPEs provides a unique capability to identify adsorbed surface species on an electrode and electrolyte, as well as map the electrode overpotentials through measurement of local surface potential. This is accomplished by measuring the kinetic energies of core-level electrons generated by x-ray irradiation. As seen in Figure 2, each element in the system produces electrons within a unique range of energies, thus fingerprinting that element. The magnitude or intensity of the signal is representative of the surface coverage. Furthermore, the degree to which the observed peaks in the PES spectra shift relative to an unbiased sample (and/or an accepted literature value) is indicative of both the local bonding environment for that element (chemical shifts) and surface potential (rigid shifts).

Presented in Figure 4 is the surface potential and chemical mapping of oxygen for a Ni/YSZ/Pt electrochemical cell



**Figure 4.** Actual map of the surface potential measured between Ni and Pt electrodes by APPEs imaging during water reduction at the Ni/YSZ interface (left). The magnitude of the surface potential is determined by measuring shifts in the photoelectron peaks for certain elements, referenced to peak positions at open circuit potential. Here there is clear evidence that the overpotential of the Ni electrode is greater than Pt, indicating the Ni electrode kinetics are less favorable. Atomic fraction of oxygen measured on Ni, Pt, and YSZ by APPEs imaging of the O 1s photoelectron peak at open circuit potential and -1.2 V (right). Decrease in the oxygen coverage is indicative of electrochemical activity that removes surface oxygenates.

operating at 973 K in a 1:1  $H_2:H_2O$  ambient at 0.5 Torr. The data are shown for open-circuit voltage and an applied bias of -1.2 V referenced to the grounded Ni electrode. A wealth of information is available from the surface potential map alone, such as the extent of ohmic loss in the YSZ and the electrode overpotential required to overcome resistance to charge transfer across the Ni/YSZ and YSZ/Pt interfaces. To our knowledge this is a first-of-a-kind observation for a high-temperature SOEC. In addition, the effect of electric bias on the oxygen coverage provides important insight into the extent to which spillover species generated at the three-phase boundary influence the thermochemical equilibrium of adsorbate coverage on the electrodes.

Thus far we have developed and established the efficacy of a unique analytical platform to investigate electrochemistry on surfaces and interfaces relevant to an SOEC, which can be adapted to other electrochemical interfaces found in capacitors and batteries (including those with liquid electrolytes). This powerful approach is capable of characterizing chemical species present on fuel-cell materials during operation, as well as determining the chemical state of electrodes and electrolytes. We anticipate that knowledge gained of the charge-transfer pathways in such systems will be a significant contribution to the electrochemical community.



## Advanced fuels and engines workshop (cont.)

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2050 timeframe. That probably seems like a long way off, but when you march back on how long it takes a set of vehicles to turn over, about 20 years, and take into account how long it takes new technology to become viable in large-scale production, we don't have much time," he said. "This workshop gives us a chance to look at engines and fuels as an entire system."

In his keynote address, Jay Keasling, chief executive officer of the Joint BioEnergy Institute (JBEI) and a UC Berkeley professor, delved into the technical details of engineering microorganisms for the production of advanced biofuels. "The technology we are developing at JBEI has tremendous power and potential for biofuel production and the kinds of molecules we can make," he said. "We are developing metabolic pathways that are tailor-made to make fuels that are identical to the petroleum-based fuels in use in our automobiles and airplanes today."

Participants then got into the heart of the workshop—panel discussions on topics like capitalizing on opportunities for biofuels in the transportation sector, the role of regulations, specifications, and standards in research and product development, and the interface between next-generation biofuels and advanced engines, followed by breakout discussions.

"As we had hoped, this workshop brought out divergent points of view on alternative fuels, the structure of the biofuel industry, and the interface between future fuels and engine development," said Ron Stoltz, manager of the CRF's Advanced Energy Initiative. "There were differences of opinion, but I think one theme that emerged is that the future is not going to be biofuels or oil, but biofuels and oil."



Jay Keasling, chief executive officer of the Joint BioEnergy Institute (JBEI) gave one of the keynote speeches. (photo by Dino Vournas)



John Dec of the Engine Combustion department leads the discussion at a breakout session of the Advanced Fuels and Engine Workshop. (photo by Dino Vournas)

Ron said a number of interesting questions came out of the workshop, like the definition of fungible fuels: Are they drop in replacements for gasoline that you would get straight from the biofuels producer? Are they compatible with the existing fuel blending and distribution infrastructure or also with the refinery process? And what is the relationship between alternative biofuels development and traditional petroleum refiners?

"On the technical side, we found agreement that current specifications for alternative fuels are not sufficiently precise to cover all potential problems and opportunities. We need a more modern approach to fuel specifications," said Ron. "On a higher level, the structure of how research is organized at the Federal level could stand some review," he says. "A more integrated approach to funding fuels and engine research might prove fruitful in the future."

A report from the Next Generation Biofuels and Advanced Engines for Tomorrow's Transportation Needs workshop will be published in the spring. he next HITEC workshop will focus on systems analysis and will take place in March.

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